

Qualitative Investigation on Hydrothermal Treatment of Hinoki (*Chamaecyparis obtusa*) Bark for Production of Useful Chemicals

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Hydrothermal treatment of an outer layer of a bark of Hinoki (*Chamaecyparis obtusa*) tree was investigated qualitatively for the possibility of utilizing residual forest biomass to produce valuable chemicals. Experiments were carried out in a semibatch reactor apparatus that allows the study of the effect of reaction temperatures in a single run. Gas chromatography–mass spectrometry analyses show the presence of useful chemicals such as furfural, aromatic compounds (1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol), and fatty acids (myristic acid, palmitic acid, and stearic acid) in the products.

KEYWORDS: Hydrothermal treatment; Hinoki; residual biomass; fatty acids; furfural

INTRODUCTION

Overdependence of the chemical industry on nonrenewable fossil fuels such as crude oil or natural gas may further increase global warming, which is detrimental to the environment. This could put lives on earth at stake if not given proper attention. To lessen the dependency of industry on nonrenewable materials, in line with the Kyoto Protocol of 1997 on climate change to reduce CO₂ emission to the atmosphere, utilization of agricultural and forest residues is being considered for production of useful chemicals. Applicable treatment technologies are sought, one of these is the use of high-temperature and high-pressure (HTHP) water.

The application of HTHP water to recover useful materials from various organic wastes, with the general purpose of mitigating environmental pollution, has recently been attracting the attention of many researchers and environmentalists. As a recognized environmentally benign solvent, the use of water offers ecological benefits for clean industrial processes. Chemical reactions in sub- and supercritical water media have attracted considerable interests (1, 2). To date, numerous articles have been written on the application to chemical synthesis and decomposition as have been summarized by Savage (3). Moreover, the use of sub- and supercritical water is an emerging technique that can provide complete decomposition of organic (4) and hazardous wastes such as PCB and dioxins (5–7). This has also been applied as a medium for recovery of useful materials from various organic wastes such as plastics (8), cellulose (9), lignin (10), and proteins (11–13).

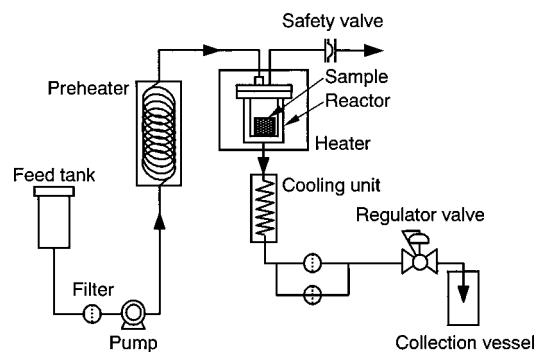


Figure 1. Schematic diagram of semibatch reactor apparatus.

Utilization of residual biomass to produce value-added chemicals by reaction in an environmentally benign and cheap solvent (i.e., HTHP water) is ecologically and industrially promising. This is investigated qualitatively in this study taking an outer layer of the bark of Hinoki tree (*Chamaecyparis obtusa*) as the sample material. Hinoki, a Japanese cypress, is a member of the “*Chamaecyparis*” family. The wild form is one of the most important timber trees, and the many cultivars are valued as ornamentals. Hinoki is possibly the most typical Japanese species, and it is used in traditional Japanese architecture. The oldest wooden building in the world, a temple in Nara prefecture, is constructed largely of Hinoki (14).

The use of the bark of Hinoki as a sample material has caught our interest because the tree is abundantly present in almost all regions of Japan and it is thought that the demand for this timber as a source of construction material will further increase. However, this does not intend to represent a wide range of agricultural and forest biomass. This preliminary investigation mainly focuses on the estimation of the optimum temperature

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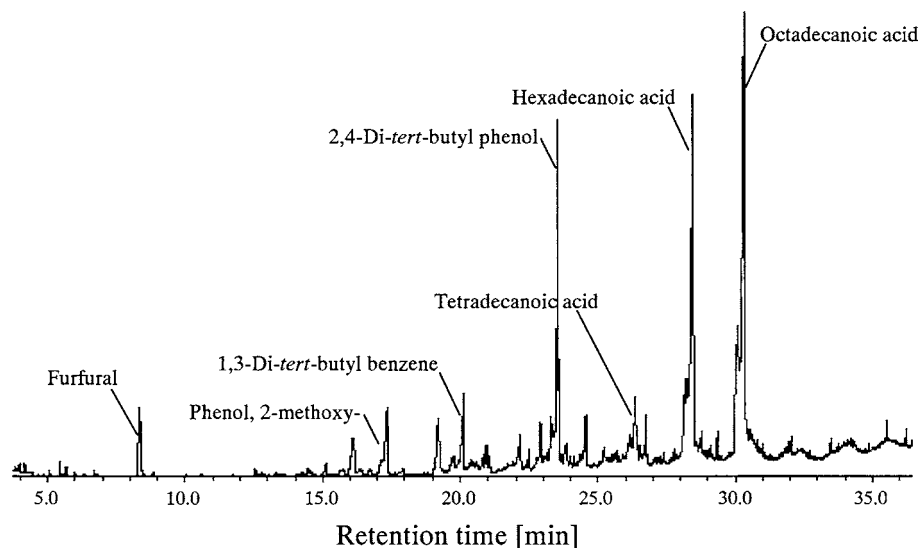


Figure 2. GC-MS chromatogram of liquid effluent obtained at 300 °C. Diethyl ether was used as the extractant.

range for the hydrothermal treatment of Hinoki bark using a novel apparatus and identification of the obtained products by gas chromatography–mass spectrometry (GC-MS) analysis.

EXPERIMENTAL METHODS

Experiments were carried out in a semibatch reactor apparatus (B-100S, Organo Corporation) shown in **Figure 1**. This apparatus, capable of investigating the effect of increasing reaction temperatures in a single run, has been described in detail elsewhere (15). This consists of a feed tank, pump, preheater, reactor, cooling unit, regulator valve, and sample collection vessel. Deionized water was delivered by high-pressure pump (NP-CX-40, NSK Corp.) at a required constant flow rate. The water passed through the preheater before entering the reactor vessel. The 100 cm³ reactor and other connecting elements were made of Inconel 625 (Ni, Cr, Mo, and Fe alloy). This was operated at a maximum temperature of 723 K and a maximum pressure of 40 MPa. A 60 mm filter was placed before the inlet pump and pressure regulator.

The outer layer of a bark of Hinoki was cut into chips of about 5 mm wide, with a thickness of about 1 mm. A 5.3 g sample was placed in the reactor. The water was allowed to flow through the reactor, and then, the temperature was set to 450 °C. The sample was collected continuously while the temperature increased, changing the sampling container after each sampling period. Extraction of the products from the aqueous mixture, for GC-MS analysis, was performed using diethyl ether.

Analyses of the products were performed using a GC-MS apparatus (Hewlett-Packard, HP5973), equipped with HP-5MS column (Hewlett-Packard, 30 m × 0.25 mm × 0.25 μm²). The sample of about 2 mL was injected into the sampling port set at 300 °C and with a split ratio of 100:1. The column temperature was set initially at 35 °C for 10 min, increased gradually to 300 °C at a rate of 10 °C/min. Helium was used as a carrier gas. The total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using a Shimadzu TOC-500 analyzer.

RESULTS AND DISCUSSION

The collected aqueous effluent appeared in single phase and did not show any evidence of the presence of two phases. Extraction with diethyl ether gave organic compounds shown in **Figure 2**, a typical GC-MS chromatogram of the products obtained at 350 °C. The major products identified with the mass spectra stored in the Wiley and NIST libraries consist of furfural, aromatic compounds (1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol), and fatty acids such as myristic acid (tetradecanoic

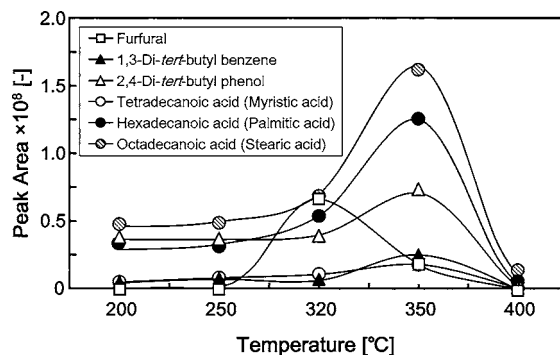


Figure 3. Effect of reaction temperature on the yield of each product based on the peak area of chromatograms.

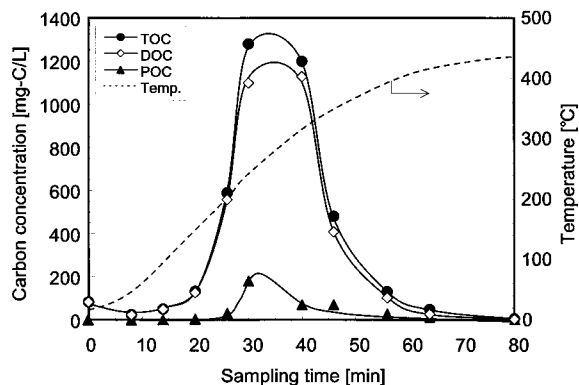


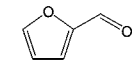
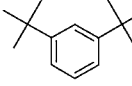
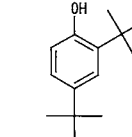
Figure 4. Carbon concentration and reaction temperature profile with time.

acid), palmitic acid (hexadecanoic acid), and stearic acid (octadecanoic acid). These compounds are mainly used as resins and antioxidants, as raw materials for the synthesis of other useful compounds, and in cosmetic industries, among others. The chemical structures and major uses of each compound are summarized in **Table 1**.

The effect of reaction temperature on the amount of products, expressed in terms of peak area, is shown in **Figure 3**. The maximum area for almost all compounds was obtained at 350 °C, except for furfural at 320 °C. It is likely that these products decomposed further at higher temperatures.

Figure 4 shows the TOC, DOC, and POC (particulate organic carbon) profile with time, along with the reaction temperature profile. POC is the difference between TOC and DOC. The TOC

Table 1. Chemical Structures of the Compounds Identified in Liquid Effluent and Their Uses

Products	Structures	Uses
Furfural *CAS [98-01-1]		Solvent, Material of furan resin and THF, Medicines, Aromatics, etc.
1,3-Di- <i>tert</i> -butyl benzene CAS [1014-60-4]		—
2,4-Di- <i>tert</i> -butyl phenol CAS [96-76-4]		Antioxidant, Resin additives, Material for organic synthesis, etc.
Tetradecanoic acid (Myristic acid) CAS [544-63-8]	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	Material of esters, Cosmetics, Surfactant, Soap, etc.
Hexadecanoic acid (Palmitic acid) CAS [57-10-3]	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	Material of esters, Cosmetics, Surfactant, Soap, etc.
Octadecanoic acid (Stearic acid) CAS [57-11-4]	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	Industrial rubber, Crayon, Plasticizer, Cosmetics, Surfactant, Soap, etc.

*CAS = CAS (Chemical Abstracts Service) registry number.

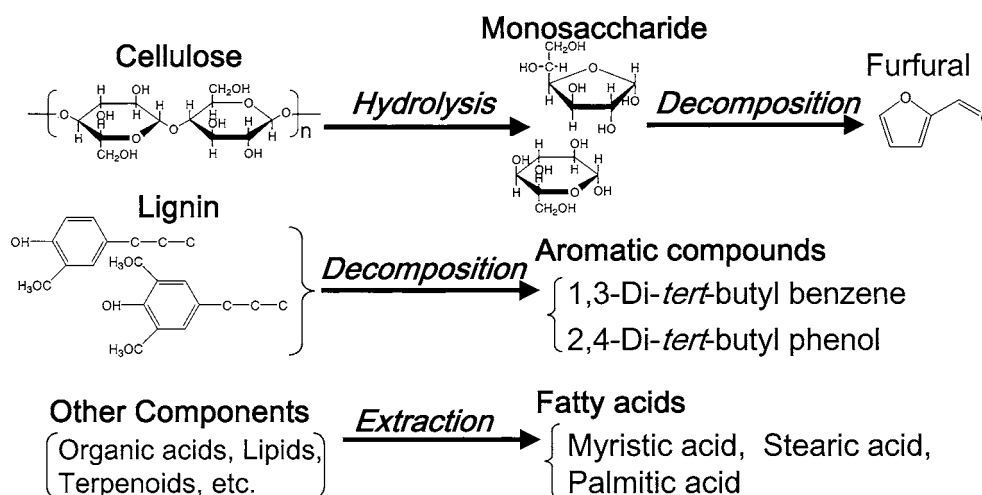


Figure 5. Speculated general mechanism of product formation.

dramatically increases between 250 and 350 °C and decreased thereafter. It is most likely that aside from extraction, the reaction took place over this region of temperature, where the ion product of water is maximum.

SPECULATED MECHANISM OF FORMATION

Wood samples have been reported to contain about 40–50% cellulose, 5–20% hemicellulose, and 20–30% lignin. The products may have been derived from these components in wood samples, and the speculated general mechanism of product formation is shown in **Figure 5**. Furfural is most likely derived from further decomposition of glucose, a product of hydrolysis of cellulose. This was also observed in the study of glucose decomposition to various useful chemicals (9, 16). Furfural could also be readily obtained from decomposition of xylan, one of the hemicelluloses. Cellulose also decomposes to yield 5-hydroxymethyl furfural, and this compound may be one of the unidentified smaller peaks in **Figure 2**. Levulinic acid, resulting from cellulose decomposition, may be another un-

identified smaller peak. On the other hand, lignin could have been decomposed to form aromatic compounds such as those identified by GC-MS—namely, 1,3-di-*tert*-butyl benzene and 2,4-di-*tert*-butyl phenol.

Hydrothermal extraction of fatty acids such as myristic acid, stearic acid, and palmitic acid could have also taken place. It is also likely that the water soluble components may contain some phenolic compounds.

This preliminary investigation lays the groundwork for further studies on the effect of various parameters on the yield of each compound and elucidation of reaction mechanism and behavior of product formation under sub- and supercritical conditions. The technique could also be applied to other wood residues.

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